Mat. Res. Soc. Symp. Proc. Vol. 740 © 2003 Materials Research Society I12.29

Simulation of Morphology and Surface Vibration in Copper and Gold Nanoparticles

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ABSTRACT

Formation and vibrational states in nanoparticles have been investigated by means of molecular dynamics simulation. The embedded atom method potentials for Cu and Au were adopted to express the interaction between atoms in the crystals. The nanoparticles were formed by cooling the atomic systems of molten states. Surface morphology of the nanoparticles were represented by highlighting the surface atoms, which were distinguished by the potential energy. Simulated surface morphology is not so symmetric as natural nanoparticles. The radial distribution function and the cross sectional view of the particles were also derived to characterize the internal structure. Thermal vibration of sample atoms at elevated temperatures was analyzed and the power spectra were calculated. Excitation of phonon mode is seen in the spectra.

INTRODUCTION

Morphology of metallic nanoparticles produced by gas-evaporation technique has extensively been investigated by means of electron microscope observations [1]. Those particles are 10-1000 nm in diameter and have highly symmetric external shape. The static morphology of these particles is strongly affected from surface energy and compared with the Wulff polyhedron. A theoretical calculation of Wulff polyhedron based on the Morse potentials has also been reported [2]. Recently, the embedded atom method (EAM) potentials have been developed [3,4], which can realize the many body nature of the atomic interaction in metals and has successfully been applied to the problems of surface and defects. Molecular dynamics simulations using the EAM potential are performed in the present study, and the process of formation and dynamical nature of the nanoparticles are investigated. The nanoparticle is a suitable system for the molecular dynamics simulation because it is consisted of manageable number of atoms by a computer. The formation of nanoparticles are related with the fundamental nature of crystal growth, and final purpose of the present study is to find the fundamental mechanisms of self-organization in the nanostructures.

METHOD OF SIMULATION

In the molecular dynamics simulation of glassy state, dynamics of 5300 atom systems are treated under free boundary condition. The motion of each atom is traced by integrating the Newton's equation of motion. The time interval Δt for the molecular dynamics simulation is chosen to be 5×10^{-15}s, which is about 1/100 of the period of the maximum atomic vibration frequency.

The potential function used in the present study has been developed by the present authors [5,6], and has been applied to the simulation of nanoparticles [7]. The potential energy for i-th atom is expressed as

$$E_i = F(\rho_i) + \frac{1}{2}\sum_{j\neq i}\phi(r_{ij}). \tag{1}$$

Where $F(\rho_i)$ is the embedding energy for i-th atom. ρ_i is the electron density function and it is a sum of the density of the neighbor atoms labeled by j. These are expressed as,

$$F(\rho_i) = D\rho_i \ln \rho_i, \qquad \rho_i = \sum_{i\neq j} f(r_{ij}). \tag{2}$$

The functions $\phi(r)$ and $f(r)$ are

$$\phi(r) = A(r_{c1} - r)^2 \exp(-c_1 r), \tag{3}$$

$$f(r) = B(r_{c2} - r)^2 \exp(-c_2 r), \tag{4}$$

where r_{c1} and r_{c2} is the truncation distance of the potential. The value of r_{c1} is chosen to be 1.65 r_0 and r_{c2} is1.95 r_0 in the simulation, where r_0 is the nearest neighbor distance. For the perfect fcc crystal, 42 atoms are involved in the present truncation r_{c2}. The other parameters are determined by fitting the potential function to the experimental values of the lattice parameter, the elastic constants, the cohesive energy, and the vacancy formation energy. The determined potential parameters for Cu and Au are shown in Table I.

Table I. EAM potential parameters

	Cu	Au
A [eV]	8289.46	5.18022×10^5
B [eV]	0.0183251	0.0183066
c_1	10.7273 r_0	15.5771 r_0
c_2	0.319759 r_0	1.28671×10^{-5} r_0
D [eV]	13.0792	11.9318

RESULTS AND DISCUSSION

Formation of nanoparticles

The process to produce copper nanoparticle is shown in Figure 1, where the external forms and the radial distribution functions are shown. Atoms on surfaces have larger potential energy

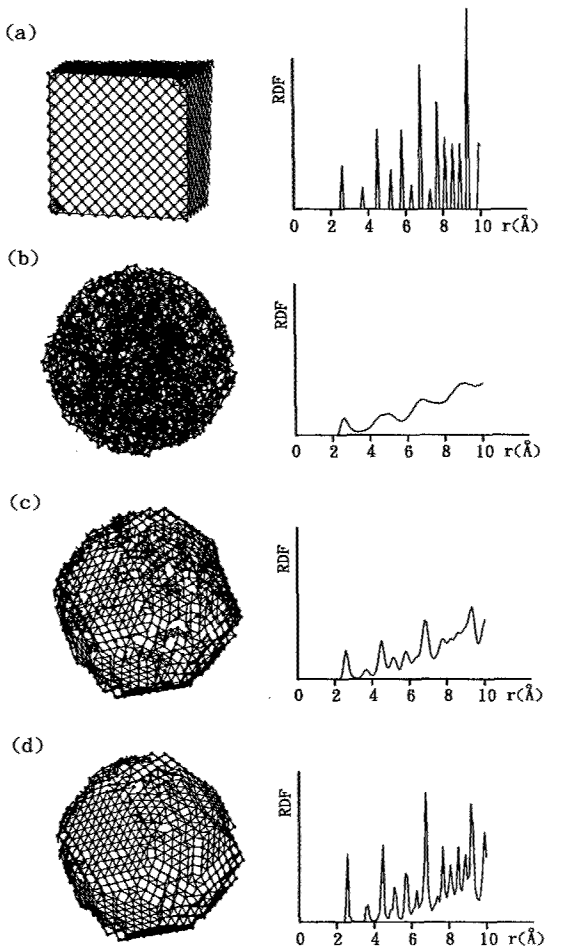

Figure 1. External form and radial distribution function in the course of producing copper nanoparticle in molecular dynamics simulation. (a) Initial fcc crystal, (b) melted state at 1470 K, (c) cooled state at 460 K and (d) final polycrystalline state at 0 K.

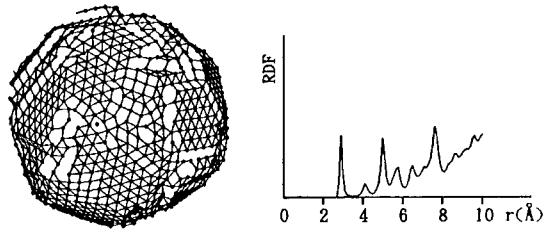

Figure 2. External form and radial distribution function of gold nanoparticle.

than internal atoms, and those are selected to show the external forms of the particle. Initially, atoms are arranged as a fcc crystal with {100} faces. When the temperature of the system is increased above 2000 K, the system is melted and external form become spherical. Then the temperature is decreased slowly at a rate of 0.02 K/step. The external form becomes asymmetrical polyhedron and the radial distribution function recovers crystalline sharp peaks with decreasing temperature. Finally obtained external surfaces of the nanoparticle is mostly covered by {111} surfaces, which has lower energy than {110} and {100} surfaces. Similar results are also obtained for gold nanoparticle, and the result is shown in figure 2. Sharpness of the RDF peak for gold nanoparticle is even dull compared with that for copper shown in figure 1. (d). This may be due to the technical problem of simulation. Heavy mass of gold atom slows down the relaxation in simulation. The cross sectional views of copper and gold nanoparticles are shown in figure 3. It is seen that the nanoparticles are consisted of several grains of fcc structure. The atoms shown by solid circles near the center and the surface of the nanoparticles are samples to monitor the vibrational states.

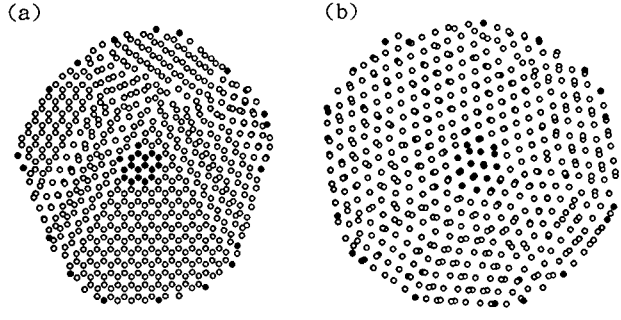

Figure 3. Cross sectional view of (a) copper and (b) gold nanoparticle.

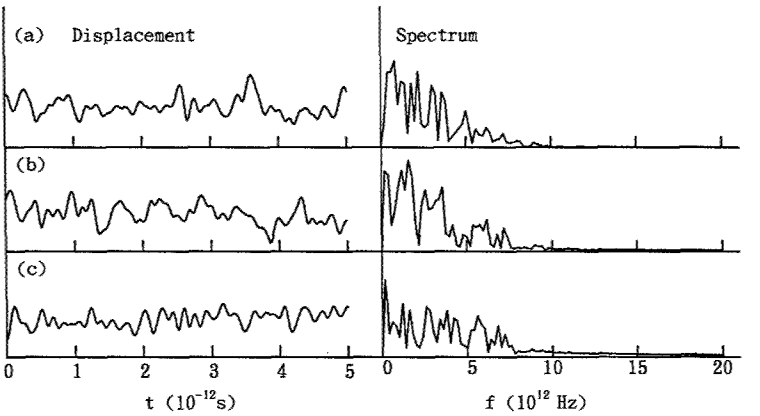

Figure 4. Examples of time variation of displacements and its power spectra. (a) Displacement of a surface atom in radial direction. (b) displacement of a surface atom in azimuthal direction , and (c) displacement of a central atoms in radial direction.

Thus obtained nanoparticles has rather asymmetric configuration than experimentally observed particles. This is due to the difference of the cooling rate. A time to cool the 2000 K sample to 0 K is about 1 ns, and this is much faster than experiments. Namely, it is difficult to attain the real equilibrium by the simulation.

Thermal vibration

Time variations of displacement of atoms are Fourier transformed and power spectra for the thermal vibration at 100 K are derived. Some examples of the displacements and power spectra are shown in figure 4. Vibrational amplitude is larger in lower frequency for surface atoms.

Mean value of power spectra for 18 sample atoms are obtained for copper and gold nanoparticles. Their logarithmic plots are shown in figure 5. Overall behavior of the spectra is inversely proportional to the frequency ($U \propto 1/f$), which is characteristic to complex or disordered systems. The solid lines in the figures show $1/f$ dependence. Vibrational amplitude deviates from the $1/f$ dependence at lower frequency, where a broad peak seems to be piled up. The peak frequency is higher for copper nanoparticle than the frequency for gold. The peak is anticipated to be due to the excitation of the thermal phonon mode. As the Debye temperature is 343 K and 165 K for Cu and Au, respectively, the frequency of thermal phonon in copper should be larger than in gold.

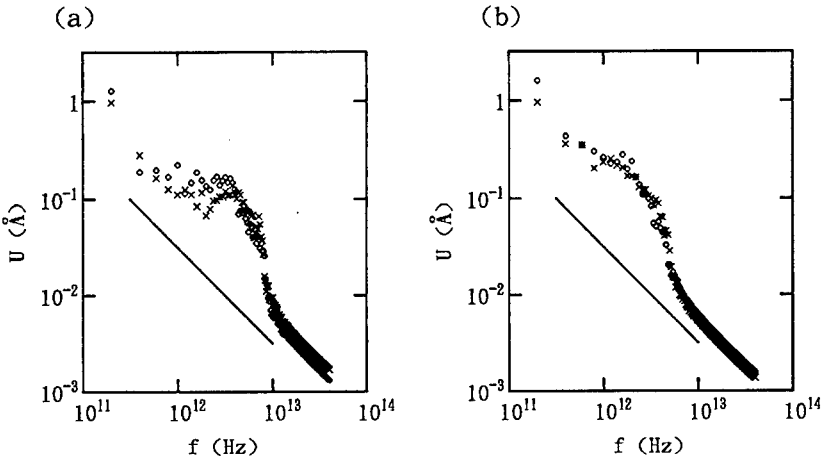

Figure 5. Power spectra of atomic vibration in (a) copper and (b) gold samples. The circles show the spectra for surface atoms and crosses for central atoms.

CONCLUSION

Formation and thermal vibration of nanoparticles were simulated. Surface morphology of simulated nanoparticles was not so symmetric as the particles experimentally produced by gas-evaporation technique. The time to form the nanoprticle in the simulation is order of 1 ns, and this may be too short the system to attain a mechanical equilibrium. The system may be a proper system to test the annealing efficiency of the simulation. The power spectra for the thermal vibration seem to consist of two components. One is phonon mode excitation and the other component is proportional to $1/f$, but the origin is not known.

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